Mixed potential theory

The mixed potential theory consists of two simple hypotheses
1 – Any electrochemical reaction can be divided into two or more partial oxidation and reduction reactions.
2 – There can be no net accumulation of electric charge during an electrochemical reaction , or in other word is a restatement of the law of conservation of charge
That is , a metal immersed in an electrolyte cannot spontaneously accumulate electric charge .From this it follows that during corrosion of an electrically isolated metal sample , the total rate of oxidation must equal the total rate of reduction.

Corrosion potential and current density
Reconsider the below anodic and cathodic reactions

$$Zn \rightarrow Zn^{+2} + 2e^-$$ (1)

And,

$$2H^+ + 2e^- \rightarrow H_2$$ (2)
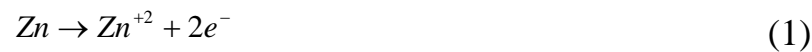
These half cell reactions occur simultaneously on the surface and each has its own half cell electrode potential and exchange current density as shown in figure (1)
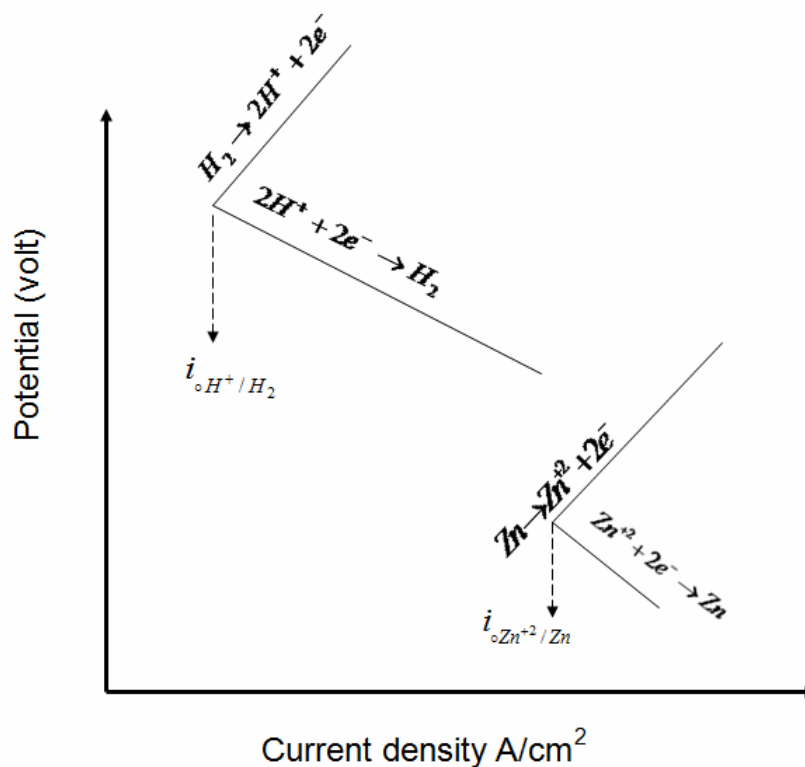

Figure (1) anodic and cathodic half cell reactions present simultaneously on a corroding zinc surface

However each two half cell electrode potential $E_{Zn^{+2}/Zn}$ and E_{H^+/H_2} cannot coexist separately on an electrically conductive surface .Each must polarize or change potential to a common intermediate value E_{corr} which is called corrosion potential . E_{corr} is referred to as a mixed potential since it is a combination or mixture of the half cell electrode potential s for reaction (1) and (2) .Hydrogen is sometimes referred to an oxidizer because it serves to "oxidize" the metal to dissolved cations by is reduction in the cathodic reaction (2) .

As reactions (1) and (2) polarize on the same surface , the half cell electrode potentials change respectively , according to

$\eta_a = \beta_a \log(\frac{i_a}{i_\circ})$ and $\eta_c = \beta_c \log(\frac{i_c}{i_\circ})$ until they become equal at E_{corr} as shown in figure (2)
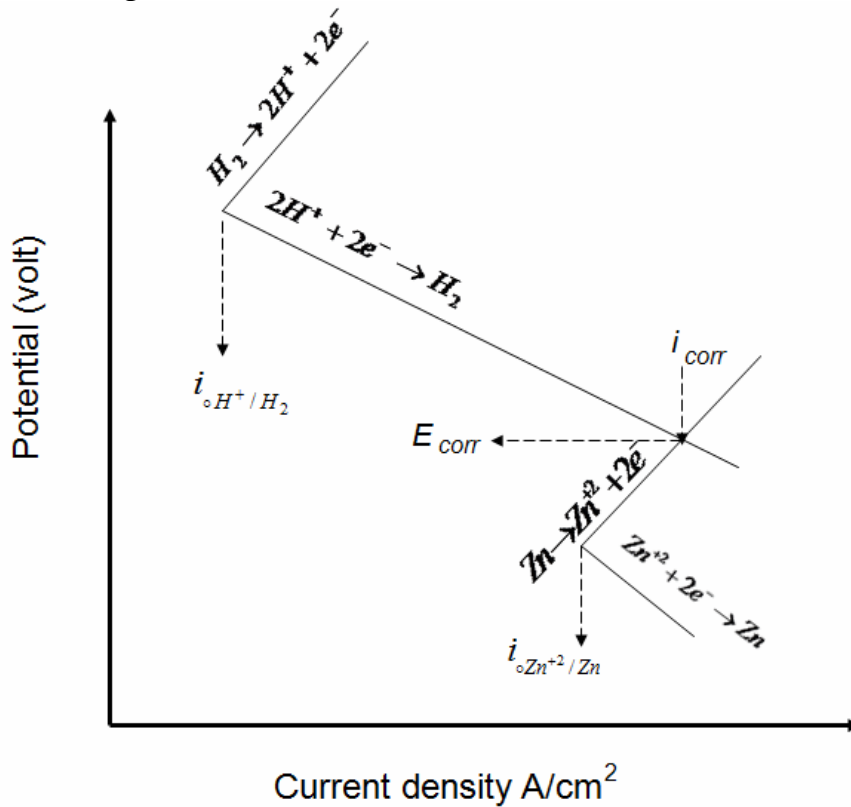

Figure (2) polarization of anodic and cathodic half cell reactions for zinc in acid solution to give a mixed potential , E_{corr} and a corrosion rate (current density).

Effect of added oxidizer

The driving force for corrosion is increased by addition of a strong oxidizer; consider the addition of mixed ferric-ferrous salts to a hypothetical metal M , corroding in an acid solution .this is a more realistic example realistic example of condition in service .Industrial acids are frequently contaminated with ferric-ferrous salts and other cationic impurities added by corrosion or unremoved during processing. Three experimental observations on the corrosion of iron result from adding oxidizer to an acid solution:

1- The corrosion potential E corr , is shifted to more noble (positive) .

2- The corrosion rate is increased.

3-The hydrogen evolution rate is reduced.

Consider the corrosion behavior of a metal M, in an acid solution containing ferric salts. This system is schematically illustrated in below figure according to mixed potential theory principles.

Log (i)
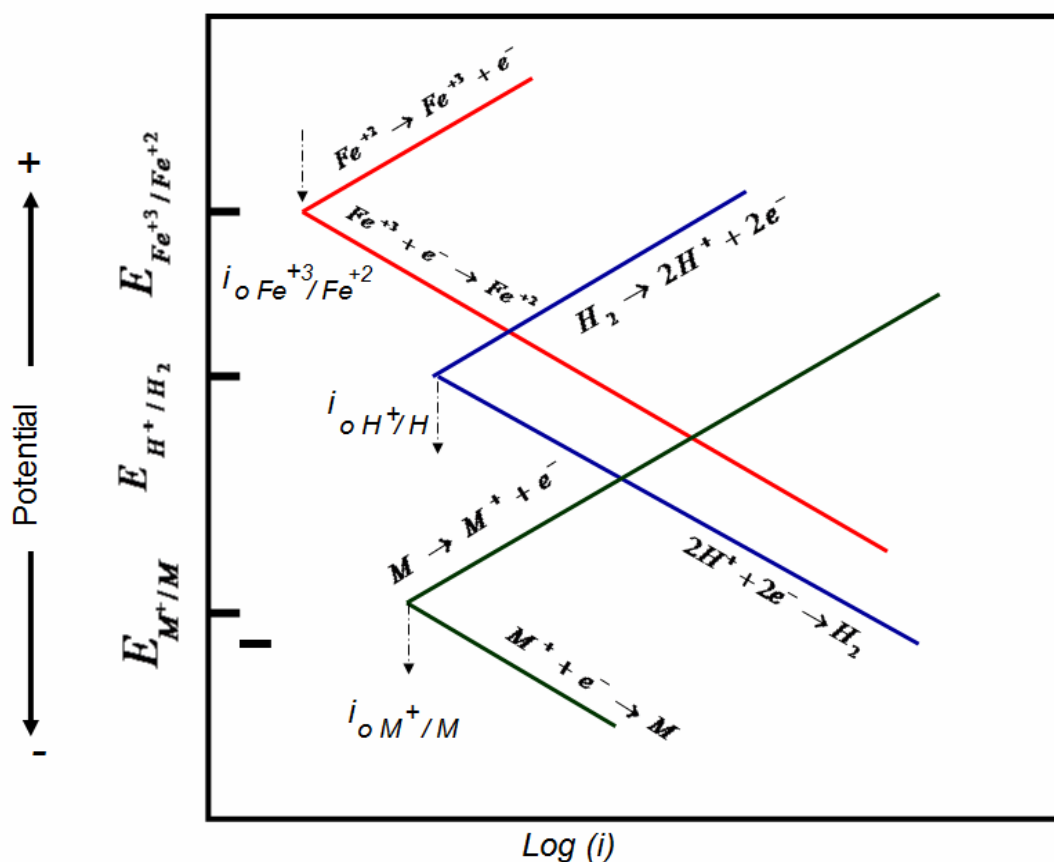
At steady state , the total rate of oxidation must equal the total rate of reduction , i.e. the total rate of oxidation is determined by summing the individual oxidation currents corresponding to metal dissolution , hydrogen-gas oxidation , and ferrous-ion oxidation at constant potentials. As shown in figure the total rate of oxidation follows the metal dissolution rate until the reversible hydrogen potential is reached and an increase is noted because of the addition of hydrogen-oxidation currents. In similar , the total rate of reduction is determined by summing total reduction currents , ferric-ion reduction , hydrogen-ion reduction and metal-ion reduction ,the point at which total rate of oxidation equals to total rate of reduction is the mixed or corrosion potential of this system. The rate of the individual processes which are occurring are illustrated in below figure . A horizontal line is drawn at E_{corr} ,the rate of metal dissolution is given by i_{corr} , equal to

$$i_{corr} = i_{(Fe^{+3} \to Fe^{+2})} + i_{(H^+ \to H_2)}$$
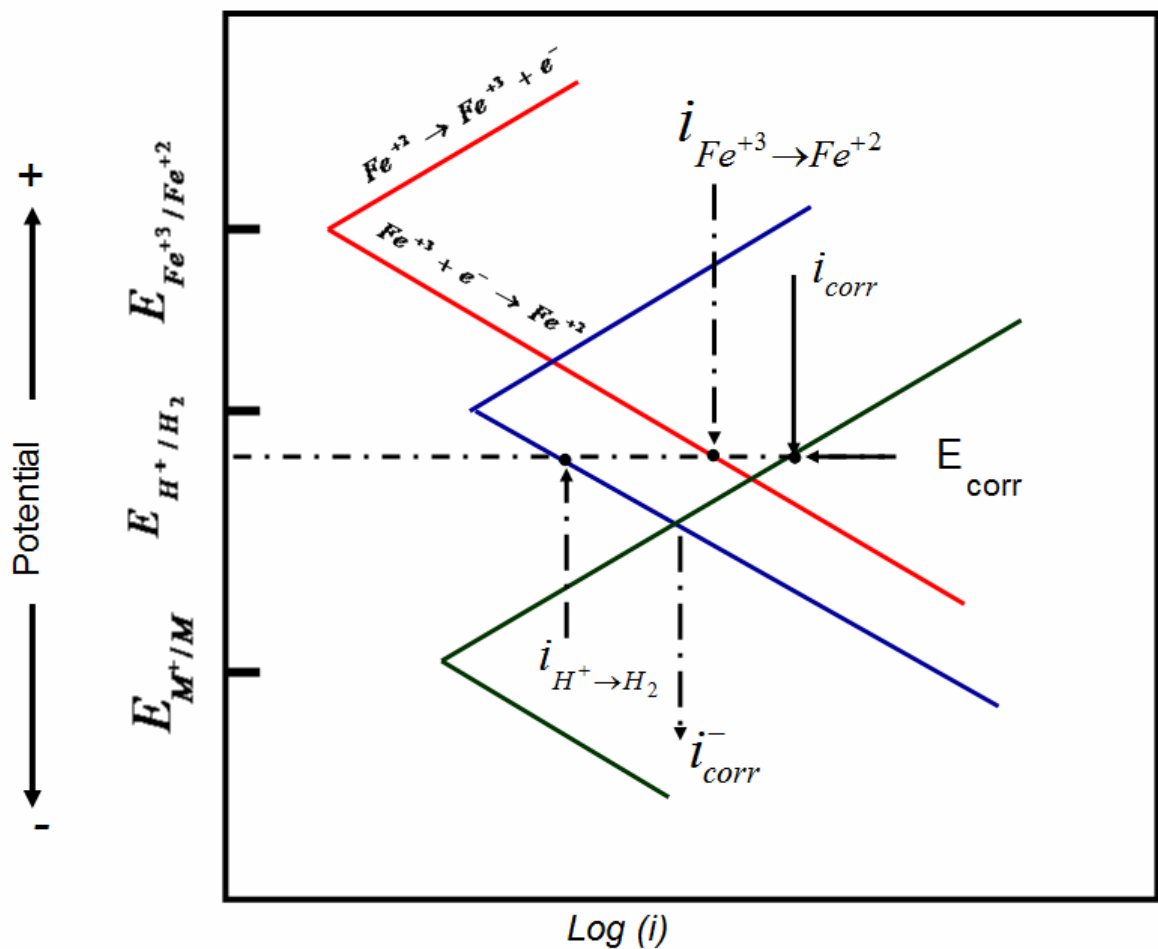
This equation satisfies the charge conservation principle of mixed potential theory.

This phenomenon has often been termed depolarization and is assumed to be the result of interactions between the oxidizing agents and hydrogen gas on the surface.

Effect of exchange current density

Mixed potential theory description of iron corrosion in acid solution is similar in appearance to that of zinc, because the half cell electrode potential for anodic reaction for iron, , is equal to about -0.44 v SHE , the corrosion rate would be expected to much lower than that for zinc , whose half cell electrode potential is much more negative , at -0.76 v SHE. The polarization diagram for zinc is showed by dashed line for comparison , the half cell electrode potential for hydrogen reduction is same for both at 0.00 v SHE and driving force for zinc is much larger than for iron , however the corrosion rate of zinc $i_{corr,Zn}$ is actually lower than that for iron $i_{corr,Fe}$ because of low current density for hydrogen reduction on zinc compared to iron
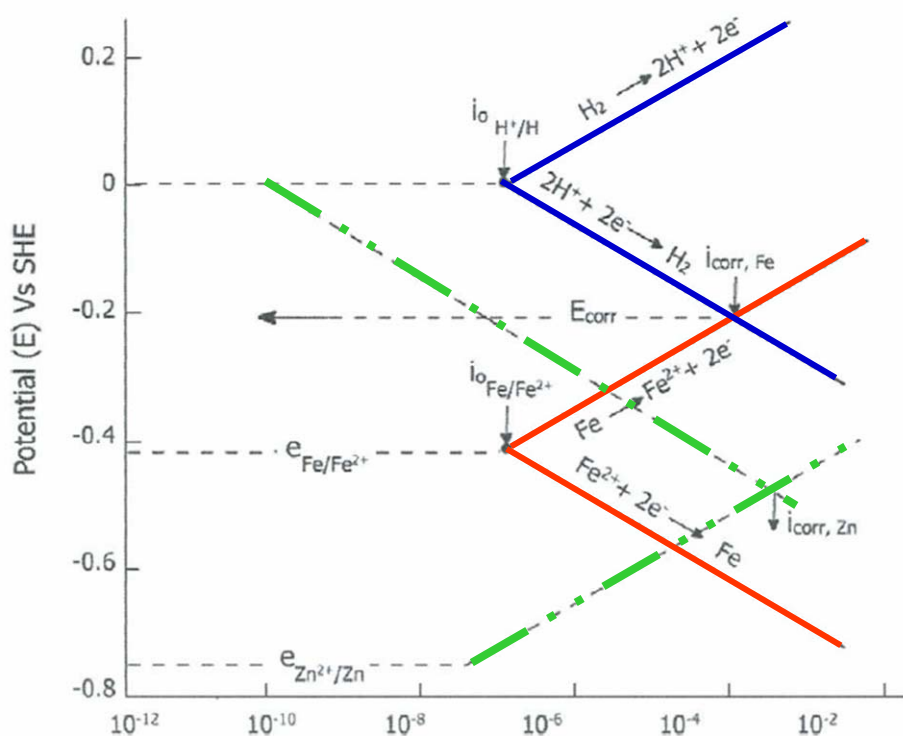
This example illustrate the importance of half cell reaction kinetics on corrosion rate and demonstrates the error that can result from drawing uninformed conclusions from thermodynamic data (i.e. half cell electrode potential)